Description and Procedures for Synchrotron Radiation, Small Molecule, Single Crystal Crystallography of Plutonium Complexes at ALS Beamline 11.3.1 (ALS and College of Chemistry Small Molecule Diffractometer)

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Direct Determination of the Structural Parameters of Plutonium Complexes by Small Molecule, Synchrotron Radiation, Single Crystal X-ray Crystallography at the ALS

A) ***The laboratory preparation and growth of the plutonium complexes (crystals) in the HERL is already covered under existing protocols of RWA 1117.*** The RWA 1117 procedure for mounting radioactive crystals follows.

Radioactive Crystal Mounting Procedure:

Equipment:
Glove Box
Parafilm
15 gauge needle
One end Sealed Quartz Capillary Tubes, 0.5mm
Rubber septa (Aldrich - size 18)
Small Plastic bag
Small Test tubes (10mm x 75mm)
Watch Glass
Magnifying lenses
Glass Fibers
Vacuum Grease
Epoxy
Nail Clippers
Putty
Jar for transport
Sally Hansen — Hard as Nails, a nylon based resin

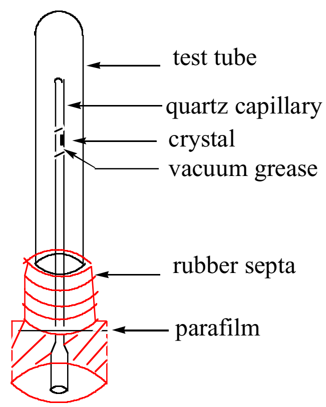


Figure 1. Test tube/capillary/septa assembly

Good Pu-239 crystals: anticipate 1 mg crystals (0.06 mCi)
maximum would be 4 mg crystals (0.25 mCi)

Methodology:

1. Prepare capillary tubes prior to working with hot materials. Place a square of parafilm on the top of the septa.
2. Run the needle through the septa with the point of the needle up through the septa.

3. Insert the capillary sealed end first through the sharp end of the needle and pull the needle out through the septa leaving the wider lip of the capillary hanging outside the septa.
4. Place the stopper on the test tube. (See Figure 1 above.)
5. Put several of these in a small plastic bag to be passed inside the glove box.

<u>Inside the glove box:</u>

6. Pass in the crystals to be mounted, the capillary tubes, and watch glass. Remove the capillary tubes in their vials from the plastic bag.
7. Place a small amount of the crystals onto the watch glass. Carefully, using the magnifying lenses and a fiber, select and isolate crystals to be mounted.
8. With a small amount of vacuum grease, adhere the crystal to the tip of the fiber and then to the side of one of the capillary tubes such that it is 1/2 of an inch from the sealed end inside the capillary.
9. Do this for at least three of each species to be mounted. Return the vials to the plastic bag for passing them out of the box.

<u>In the hood:</u>

10. Remove the capillary from the tube using the septa as a handle. The capillary will be surveyed for activity with a suitable hand held alpha survey instrument since direct swipe will not be practical. Only capillaries that have non-detectable, external alpha contamination will be suitable for continued use and this will be documented.
11. Gently, cut the capillary with the nail clippers to approximately 1 to 1 1/2 inches in length. <u>Caution:</u> Keep an eye on the crystal. The goal is to shorten the tube for mounting.
12. Seal the open end of the capillary with epoxy.
13. Place the sealed crystal into the putty on a flat surface (such as the lid of the container for transport) such that the freshly sealed end can dry in air.
14. Prior to commencing the encasement in "Hard-as-Nails" (see Figure 2), the capillary will be once again surveyed for activity with a suitable hand held alpha survey instrument since direct swipe will not be possible. Only capillaries that have non-detectable, external alpha contamination will be suitable for use and this will be documented. Allow a couple minutes to dry. Paint the outside of the capillary with the Hard-as-nails. This will dry hard. This nylon based resin will hold any pieces of the glass and crystal together in one piece should the capillary somehow be dropped or crushed. A small red thread will be permanently attached to the capillary when the "Hard-as-Nails" coating is applied. This makes locating the capillary, should it be miss-handled, much easier. Once the nail coating has dried, a "Post-it" flag will be attached to the capillary as well. Prior to mounting on the goniometer assembly, the capillary will once again be surveyed by a certified alpha survey probe.

Figure 2. "Hard as Nails"

B) The transfer of the plutonium crystals in the HERL from the growth containers to the quartz capillaries that will be used as primary containment in the x-ray diffraction (XRD) measurements is a new activity. This forms the first part of the amendment to RWA 1117 for this work. Note that similar procedures are being used successfully at Los Alamos National Laboratory for laboratory-based XRD measurements.

The capillary containing the plutonium crystal will be mounted on the XRD goniometer. The capillary will be mounted on a standard post with wax and rubber cement adhesive (see Figure˚3). The height of the crystal will be adjusted to that required by the Beamline 11.3.1 diffractometer (which is about 69˚mm total from the base of the goniometer mount). A picture will be taken and placed in the laboratory notebook of the goniometer mount and capillary assembly. The goniometer mount will be indicated on the body as to the location of the alignment slot to make insertion into the diffractometer straightforward.

Figure 3. Rubber cement and was for mounting capillary to the post.

The goniometer-capillary assembly (GCA) will be surveyed by certified alpha and β-γ survey instruments. The results will be recorded. The goniometer base itself will be carefully swiped and counted in the HERL Ludlum 2929. If non-contaminated, work will proceed. The GCA base will be screwed into the plastic goniometer container and the threaded seal region taped to ensure that no material could escape. The goniometer container will be indicated with the appropriate radioactive labels. The exterior of the goniometer container will be swiped and certified as non-radioactive using the HERL Ludlum 2929. A plastic bag will be placed around the goniometer container and sealed. The plastic bag with the GCA will be placed in a tight-fitting ice cream carton and sealed for transport to the ALS. The ice cream cartoon will be swiped and established as non-radioactive prior to transport to the ALS. Permission to proceed with the experiments at the ALS must be received before transporting the GCA to the ALS and the ALS Associate Health Physicists/Radiological control Technician-Brian Fairchild notified (x6212). The material must be transported to the ALS in accord with RWA 1117 restrictions.


Figure 4. Goniometer container.

C) ***Direct Determination of the Structural Properties of Plutonium Complexes by Small Molecule, Single Crystal, Synchrotron Radiation X-ray Crystallography at Beamline 11.3.1 at the ALS***. This is a new activity that is being incorporated into RWA 1117 to permit XRD characterization of the plutonium complexes at the ALS. Since the XRD work will use contained radioactive materials, it is more appropriate to associate the XRD activities with RWA 1117 rather than RWA 1007 which addresses in-vacuum experiments at the ALS with radioactive materials.

Brief Summary of ALS Experimental Activities

Location:	Beamline 11.3.1
Experiment:	Small molecule, single crystal XRD in the 11.3.1 hutch
Beamline Contact:	Al Thompson (x5590)
EH&SRCT/HP Contact:	Brian Fairchild (x6212)

The plutonium complex will be contained in a quartz capillary for the measurements. The quartz capillary will be the primary containment for the crystal and the use of such capillaries is common for small crystals, especially with radioactive materials, in XRD. A special nail polish will be applied to the outside of the capillary to form a second layer of containment or barrier, but primarily to prevent the capillary from both being broken in a catastrophic fashion and the material leaking out. In fact, similar procedures are being used successfully at Los Alamos National Laboratory for laboratory-based XRD measurements. Should the capillary drop, an affixed red thread will make finding the capillary easy. A "catcher" is being designed for the small molecule crystallography stage so that if the capillary becomes detached from the goniometer mount post, it will fall into one of these two trays for safe and easy recovery. During the experiment, the hutch will be designated as an RMA and before returning to general use, will have to be released by the RCT/HP. Since the sample is a multiply contained solid with a special anti-fracture coating and the experimental area will be designated as an RMA, should there be an unexpected occurrence, there would be no personnel and procedural ramifications. All handling of the plutonium crystals at the ALS will be done in the presence of the ALS RCT/HP or the RCT/HP designate.

We have gone through a dry run with Al Thompson on 14 May 2003 at Beamline 11.3.1 with a non-radioactive crystal so that we could prepare and understand what is entailed for the actual radioactive experiments. Another non-radioactive crystal will be prepared in this manner for testing at Beamline 11.3.1 with Al Thompson during the first week of June 2003. This will ensure proper data collection from capillaries and will double check that there will be no collisions with the capillary.

Amount of material at the ALS: One crystal at a time, except for loading and unloading operations at which time we would like to be able to unload a sample and load another without having to return to the HERL (two samples on the floor during loading/unloading operations but only one open at a time). The total amount of Pu-239 in a single crystal plutonium complex will not be greater than 4 mg and this number is very conservative. The amount of Pu-239 in these crystals should be much less than this. This translates into a maximum activity for each crystal of 2.5 x10^{-4} Ci, ~1 x10^{5} dps (Pu-239 SpA=0.06204 Ci/g, alpha-emitter). The Pu-239 used in these complexes is isotopically quite clean, although there will be the accompaniments of 238, 240, 241, 242-Pu and Am-241 (lower than usual levels resulting from clean source of Pu-239).

The ALS Experimental Form, the Experimental Hazards Form, and the Radioactive Materials Form will be completed for these experiments.

General ALS Procedures

All handling of the plutonium crystals at the ALS will be done with the ALS RCT/HP or designate present. Standard radiological precautions and safety procedures will be employed. The usual complement of personal protective equipment will required to handle the materials at the ALS (gloves, coat, glasses, and TLD badge).

The detailed preparation of the plutonium (Pu-239) crystals for XRD, has been described as above, to obtain permission to grow the plutonium crystals and to prepare them for XRD measurements under RWA 1117 in the HERL prior to any ALS work. It is important to note that similar procedures are being used successfully at Los Alamos National Laboratory for laboratory-based XRD measurements. The procedures to be used at the ALS have been developed along with input and interaction of Al Thompson, the Beamline 11.3.1 scientist. Beamline 11.3.1, the location of the XRD experiments at LBNL, is a joint ALS and University of California, College of Chemistry beamline facility. The radioactive material will be double-contained and used under ambient conditions (except for nitrogen jet cooling).

The plutonium crystals will be mounted in sealed capillaries for the XRD work at ALS Beamline 11.3.1. The exterior of the capillary will not be radioactive. The capillary will then be coated with "Hard-as-Nails" polymer coating that will prevent catastrophic failure of the quartz capillary and release of material. Furthermore, this provides an additional barrier. During the experiments, the x-ray hutch also provides an additional level of isolation and access control. A red thread will be attached to the capillary coating to ensure convenient visual location in case of an unexpected event. The entire sample assembly will be brought to the ALS intact to minimize the amount of handling at the ALS. We have run several failure tests of XRD capillaries coated with "Hard-as-Nails" at LBNL to establish that it will be effective in the case of an unexpected event. Its use for this purpose has been approved at Los Alamos National Laboratory. The results of these tests are shown in Figure 5, images a-f. The sealing properties of the capillaries and another simulated event are illustrated in Figure 6, images a-d. The goniometer head with the brass holding post that mounts the coated capillary (via epoxy and wax) is shown in Figure 6e. The top picture in Figure 6e shoes the goniometer mount screwed into the base of the plastic goniometer container. A clear plastic shroud also screws onto the threads of the base. This provides sufficient clearance for a mounted capillary and forms an excellent transporter for the goniometer-capillary assembly (GCA) and the completely assembled unit has been shown previously in Figure 4.

Amount of material at the ALS: One crystal at a time, except for loading and unloading operations at which time we would like to be able to unload a sample and load another without having to return to the HERL (two samples on the floor during loading/unloading operations but only one open at a time). The total amount of Pu-239 in a single crystal plutonium complex will not be greater than 4 mg and this number is very conservative. The amount of Pu-239 in these crystals should be much less than this. This translates into a maximum activity for each crystal of 2.5 $x10^{-4}$ Ci, ~1 $x10^{5}$ dps (Pu-239 SpA=0.06204 Ci/g, alpha-emitter). The Pu-239 used in these complexes is isotopically quite clean, although there will be the accompaniments of 238, 240, 241, 242-Pu and Am-241 (lower than usual levels resulting from clean source of Pu-239). The ALS Experimental Form, the Experimental Hazards Form, and the Radioactive Materials Form will be completed for these experiments.

A temporary RMA will be set up and posted at ALS Beamline 11.3.1 to unload the goniometer-capillary assembly (GCA) from the ice cream cartoon. The GCA will be examined through the clear plastic container upon arrival to ensure that the GCA is intact before unloading the GCA from the container. The GCA will be inverted vertically for several minutes to ensure that the capillary is well-affixed to the GCA post after transport. Upon removal of the GCA from the container, the GCA will be monitored with survey meters as will the inside of the goniometer container. The standard ALS radioactive materials emergency response kit and meters assigned to the ALS will be utilized. Any waste materials generated will be transported back to the HERL for disposition or will disposed of by the RCT/HP.

The access to the BL-11.3.1 diffractometer goniometer mount will be cleared by remotely moving both the nitrogen jet cooling and the beam stop apparatus away from the goniometer head mount with the modular small molecule diffraction stage that will be utilize for the measurements. A "catcher" is being designed for the small molecule crystallography stage so that if the capillary becomes detached from the goniometer mount post, it will fall into one of these two trays for safe and easy recovery. The catcher platforms will be assembled and put in place. At this time, the BL-11.3.1 x-ray hutch will be posted as an RMA and the GCA attached to the diffractometer mount. Note that there has been a dry run of this procedure without the catcher trays on the 14th of May 2003 with Al Thompson at the beamline. The location of the mounting slot on the GCA will have been indicated to make mounting to the diffractometer straightforward. Using the test GCA assembly, there was no problem safely mounting to the diffractometer receiver although some dexterity is required. Should the entire GCA be fumbled during this procedure, it would likely ruin the capillary (without rupturing) but there would be no additional consequences other than ending the current experiment. The "Post-it" flag will be removed from the capillary, leaving just the red thread as a visual aid. The temporary RMA outside of the Beamline hutch will be surveyed and decommissioned.

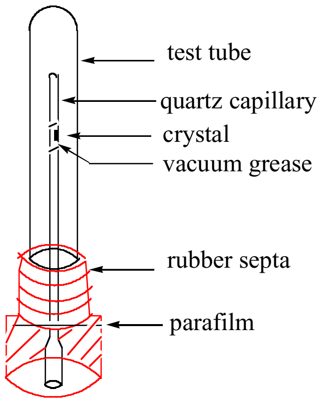
Once the GCA is mounted to the diffractometer, the nitrogen jet and beam stop apparatus will be moved back into place. The final alignment of the capillary with respect to the beam will be accomplished via video camera. Should any fine height or xy positioning of the capillary be needed, this can be done easily via the goniometer mount adjustments. Once this has done, data collection may proceed once approved by the beamline scientist responsible for data collection. The nitrogen jet stream cooler will be used and these have been used with capillaries before and this will not cause problems with the "Hard-as-Nails" coating. Of course, the x-ray hutch must be closed to enable the x-rays, thus limiting access to the diffractometer and GCA. This adds an additional barrier to contact and access to the plutonium crystal. During data collection, there are no collision hazards. This will be further established during tests with a non-radioactive crystal in the exact same capillary system that will take place in the first week of June 2003.

Once the GCA is mounted, an inspection of the GCA integrity will be performed prior to entering the hutch by remote video camera.

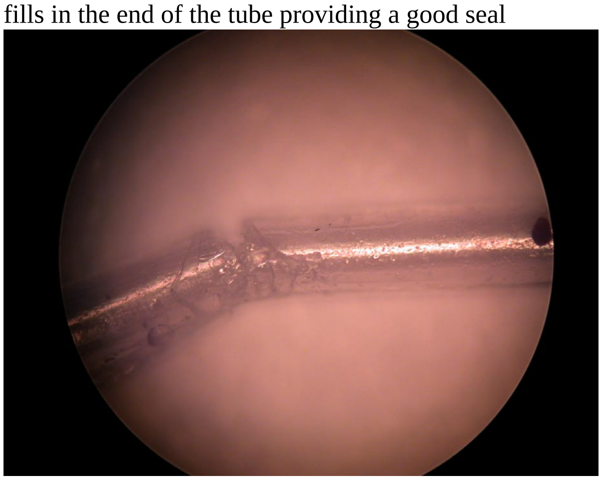
Once data collection has been completed, the GCA will be removed in a similar, but reverse manner to its installation. Before removal, the GCA assembly will be inspected to make sure that it is intact before removal from the diffractometer mount. The external RMA will be set up to receive the GCA. The GCA will be surveyed, placed into the plastic container, sealed, bagged, an placed into the ice cream carton. The instrumentation in the x-ray hutch in close proximity will be surveyed and swiped. Should this be the only or final sample, the surveys and documented swipes will be used to release the Beamline 11.3.1 hutch to non-radioactive general use and will be de-posted by the RCT/HP. There will be no general access to the hutch until it has been formally released. There is no need to have a researcher present during the entire data collection process unless so desired as there is sufficient access control unless desired by the beamline scientist. Should another sample be ready for characterization, the loading process will be initiated and the formal release activities performed only at the end of the entire experimental run. Once all samples have been transported from the ALS, the temporary external RMA will be surveyed and de-posted.

Emergency procedures: The standard emergency response information will be posted at the beamline along with RWA and the contact information of the researchers. Should unanticipated condition arise during the procedures, the experiment will hold and contact the RCT/HP prior to proceeding further.

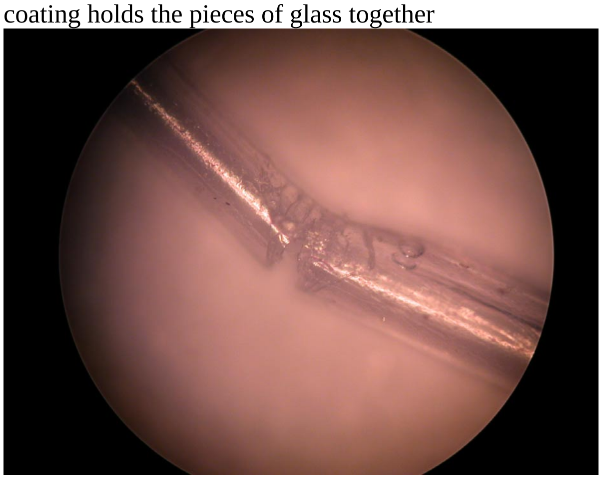
Figure 5. Enlarged views of a 0.5 mm capillary tube sealed with Devcon – 5 minute epoxy, coated with a protective layer of the nylon based resin (Sally Hansen's Hard-as-Nails®) containing a crystal of 3-hydroxy-2-pyridinone propylamide (PR-Me-3,2-HOPO)



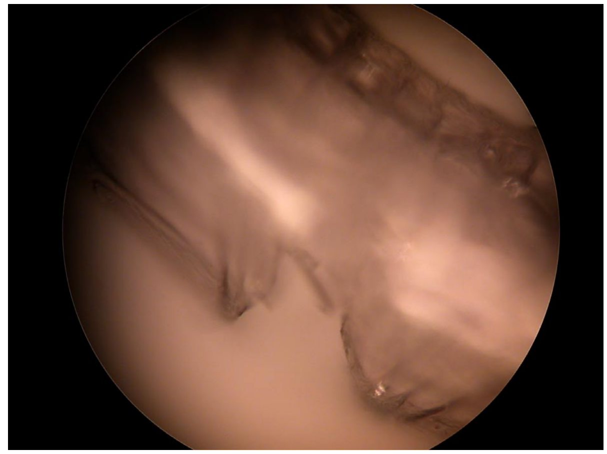
a) the sealed end of the capillary, note how the epoxy fills in the end of the tube providing a good seal



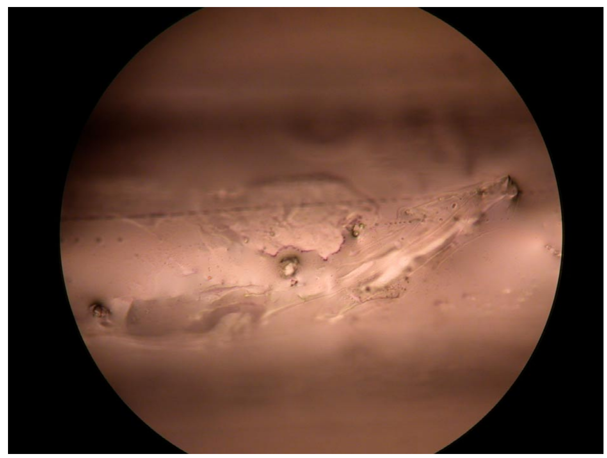
b) a break in the capillary – note how the fiberous coating holds the pieces of glass together



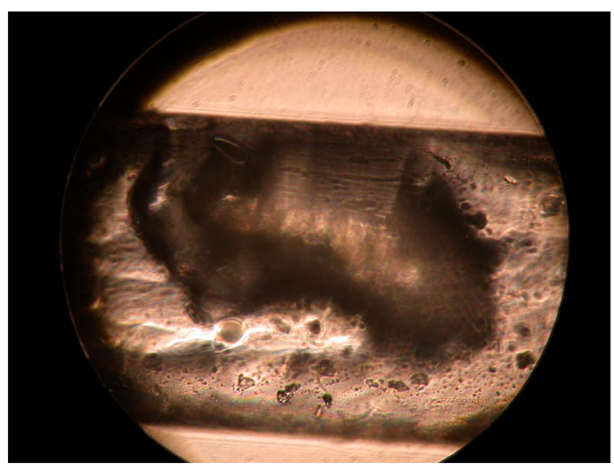
c) another view of the break in the capillary makes the tear in the coating more evident



d) enlarged view of c)

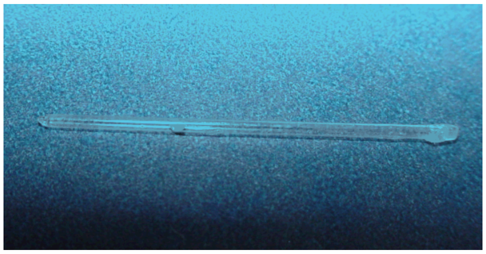


e) The crystal inside the capillary in silicon grease



f) The reverse view of e) makes it easier to see the translucent crystal

Figure 6.

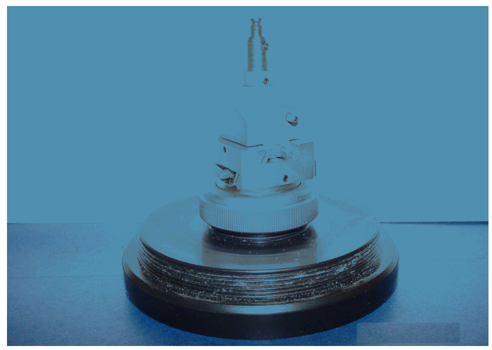


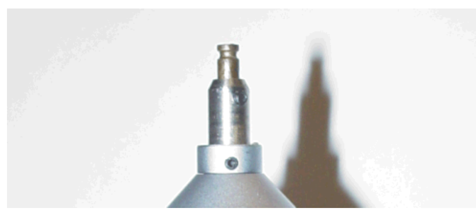
a) In this image, we have a 0.5 mm capillary, approximately 3cm long tube with a yellow-gold crystal sealed inside.

b) A close-up of the sealed end of the above capillary tube. The epoxy completely fills in and covers the opening, this prevents losing the cap on this end.

c) This capillary after a simulated accident. Representative of what might happen if dropped or stepped on, this capillary was crushed with a rubber mallet. Notice how the structure remains intact due to the outer nylon coating. This piece is actually quite flexible and can be bent and twisted while remaining intact.

d) This is a close up view of the above crushed capillary. Notice how the crystal is also crushed, but remains localized and contained by the capillary.





e) (above) The goniometer head on which the capillary will be mounted. This will then be used to align the crystal at the x-ray diffractometer in 70A prior to transfer to the ALS. The capillary fits snugly into the brass pin and secured with wax. This can be adjusted with the screws on the side of the goniometer. The goniometer screws into the black base which in turn has a clear plastic cover for transport. The entire assembly can then be placed in an insulated steel paint can for transportation between facilities.
f) A close-up of the brass holding pin.

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Page last updated
March 20, 2003

Beamline 11.3.1

Small-Molecule Crystallography

Operational	Now
Source characteristics	Bend magnet
Energy range	6-17 keV
Monochromator	Channel-cut Si(111)
Calculated flux (1.9 GeV, 400 mA)	4×10^{12} photons/s/0.01%BW at 12 keV
Resolving power (E/ΔE)	1000
Endstations	Medium-sized hutch with optical table
Detectors	Large-area x-ray scintillator/CCD detector
Spot size at sample	250 μm x 100 μm
Samples	
Format	Crystals as small as 15 μm x 15 μm x 15 μm
Preparation	Crystals are mounted on standard goniometer head
Sample environment	Air
Special notes	Bruker SMART software is used for diffraction analysis
Experimental techniques	X-ray diffraction and small-angle scattering
Scientific applications	Crystal structure of compounds
Local contact/Spokesperson	Name: Al Thompson Affiliation: Advanced Light Source, Berkeley Lab Phone: (510)486-5590 Fax: (510) 486-7696 Email: acthompson@lbl.gov
Beamline Phone Numbers	(510) 495-2117

More information about small-molecule crystallography at the ALS is available at the Beamline 11.3.1 Web site.

Table of all beamlines
Diagram of all beamlines